Size and Composition Distribution of Airborne Particulate Matter in Northern California: I—Particulate Mass, Carbon, and Water-Soluble Ions

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ABSTRACT

The San Joaquin Valley (SJV) in California has one of the most severe particulate air quality problems in the United States during the winter season. In the current study, measurements of particulate matter (PM) smaller than 10 μm in aerodynamic diameter (PM_{10}), fine particles ($PM_{1.8}$), and ultrafine particles ($PM_{0.1}$) made during the period December 16, 2000–February 3, 2001, at six locations near or within the SJV are discussed: Bodega Bay, Davis, Sacramento, Modesto, Bakersfield, and Sequoia National Park. Airborne $PM_{1.8}$ concentrations at the most heavily polluted site (Bakersfield) increased from 20 to 172 μg/m^3 during the period December 16, 2000–January 7, 2001. The majority of the fine particle mass was ammonium nitrate driven by an excess of gas-phase ammonia. Peak $PM_{0.1}$ concentrations (8–12 hr average) were ~2.4 μg/m^3 measured at night in Sacramento and Bakersfield. Ultrafine particle concentrations were distinctly diurnal, with daytime concentrations ~50% lower than nighttime concentrations. $PM_{0.1}$ concentrations did not accumulate during the multiweek stagnation period; rather, $PM_{0.1}$ mass decreased at Bakersfield as $PM_{1.8}$ mass was increasing. The majority of the ultrafine particle mass was associated with carbonaceous material. The high concentrations of ultrafine particles in the SJV pose a potential serious public health threat that should be addressed.

IMPLICATIONS

Current regulations exist for airborne PM_{10} and fine (PM2.5) particle mass, but research suggests that $PM_{0.1}$ may have equally serious health effects. Peak $PM_{0.1}$ concentrations in California's SJV are among the highest in the United States. $PM_{0.1}$ concentrations in the SJV did not increase during a multi-week stagnation episode, even though $PM_{2.5}$ concentrations during the same time period increased by a factor of 7. Nighttime concentrations of ultrafine particles were twice as large as daytime concentrations. The sources of ultrafine particles and the mechanisms that govern their behavior need to be identified to protect public health.

INTRODUCTION

Central California routinely experiences some of the highest concentrations of airborne particulate matter (PM) found in the United States.[1–7] The San Joaquin Valley (SJV), located in the lower half of central California, has been in violation of the National Ambient Air Quality Standards (NAAQS) for airborne PM smaller than 10 μm (PM_{10}) in aerodynamic diameter since their inception in the Clean Air Act Amendments of 1990.[8] The American Lung Association recently identified three of the four most polluted U.S. cities as being in the SJV.[9] Approximately 3 million people live in the SJV, with future growth expected. As the population in the SJV continues to increase, the serious public health problem caused by particulate air pollution in the region must be addressed.

The first step in the solution to any air quality problem is the characterization of the spatial and temporal trends for the pollutant of interest. Airborne PM is a complex pollutant consisting of many individual solid particles or liquid drops that each have a unique size and chemical composition. Recent studies designed to identify the relationship between airborne PM and health effects have focused on coarse (PM with aerodynamic diameter between 10 and 2.5 μm), fine ($PM_{2.5}$; PM with aerodynamic diameter less than 2.5 μm), and ultrafine ($PM_{0.1}$; PM with aerodynamic diameter less than 0.1 μm) particles.[10–18] One study suggests that the health effects of fine and ultrafine particles may be independent of one another.[14] The composition of airborne PM in each of these size fractions must be characterized to identify potential threats to public health.

During the period December 2000–February 2001, the California Regional Particulate Air Quality Study was conducted in central California to better characterize airborne PM in the SJV. As part of that study, airborne PM samples were collected at five locations using filter samplers and cascade impactors so that the full composition distribution of airborne PM could be studied in all relevant size ranges. The purpose of this paper is to report the

mass and composition of airborne PM measured in the PM_{10}, $PM_{1.8}$, and $PM_{0.1}$ size fractions. The concentrations of organic compounds (OC), elemental carbon (EC), and water-soluble ions will be discussed; future analyses will identify the results of trace metal and trace organics in each size fraction. The spatial and temporal patterns revealed by this analysis will provide useful information for inhalation exposure studies and will support source apportionment analysis. Size-resolved analysis has been performed in the Los Angeles area[19–23] for many years, but relatively few studies have been conducted for the SJV. The current study represents the first time that the composition, spatial, and temporal trends of coarse, fine, and ultrafine particles have been studied simultaneously at multiple sites in the SJV. To the authors' knowledge, the current study constitutes the largest measurement of size-resolved ambient PM concentrations using cascade impactors outside of Los Angeles.

BACKGROUND

Figure 1 shows the Sacramento Valley and the SJV that combine to form California's Central Valley. The Central Valley stretches from Bakersfield in the south to Redding in the north (a distance of ~800 km). It is completely enclosed by the Coastal Mountains to the west and the Sierra Nevada Mountains to the east. The San Francisco Bay Delta provides the only break in the surrounding mountains at the Carquinez Strait. Further to the south in the coastal ranges, the Altamont Pass (304 m), Pacheco Pass (427 m), and Cottonwood Pass (610 m) constitute the lowest connections between the ocean and the SJV.

During the winter months, a meteorological phenomenon named the Great Basin High occurs in California.[1,3] High pressure aloft causes elevated temperatures above 850 millibars (mb) and weak pressure gradients between the coast, the SJV, and the Mojave Desert. When a Great Basin High occurs and overnight ground-level temperatures in the SJV decrease to less than 5 °C, atmospheric mixing depths become low, especially during the night. This condition traps pollutants close to the Earth's surface, effectively putting a lid on the lower layer of the atmosphere in the enclosed valley where pollutants can build up over several days or weeks. During December, January, and February, rains suppress the production of windblown dust in the SJV. Fine particles and their precursors continue to be emitted, however, and it is during these winter months that the NAAQS for PM_{10} and $PM_{2.5}$ are exceeded significantly.
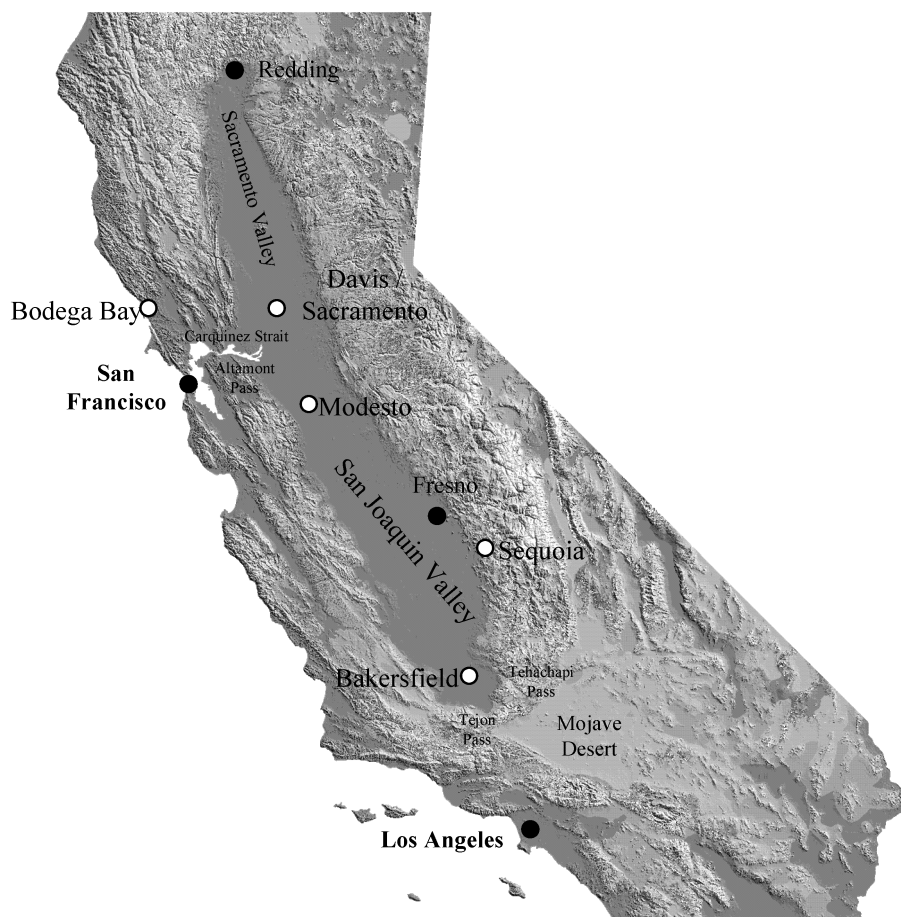

Figure 1. California's Central Valley and the sampling locations used in the current study (marked with open circles).

A conceptual model has been suggested[1,3,24,25] to better understand the processes that create PM exceedences during wintertime Great Basin Highs: A shallow inversion layer with a depth of 30–50 m is created at night in which wind speeds are less than 1 m/sec. Nighttime emissions of primary PM and precursors to secondary PM can accumulate to high concentrations in this inversion layer. Above the surface layer (i.e., ~50 m above ground level [agl]) wind speeds of 1–6 m/sec occur, but direction is highly variable. This increased wind speed allows transport of the upper layer air mass over distances of 50–300 km during the ~18 hr that the nighttime inversion lasts (from ~5:00 p.m. to 11:00 a.m.). In the daytime, the sun heats the valley surface and breaks down the inversion by ~11:00 a.m. This creates a single valley-wide layer believed to reach 500-2000 m agl. The creation of this single layer dilutes the pollutants built up in the shallow inversion layer and promotes mixing throughout the valley. The cycle of shallow nighttime inversions and daytime coupling continues for days or weeks until the stagnation created by the Great Basin High is broken by a deep trough that traverses the region in the form of a winter storm. In this fashion, the SJV air is cleaned and mixed with the air of neighboring airsheds, bringing an end to the episodes of high airborne PM concentrations.

The composition and spatial and temporal trends of precursor gases, PM_{10}, and $PM_{2.5}$ have been investigated previously during the San Joaquin Valley Air Quality Study conducted in 1990[2,26] and the Integrated Monitoring Study conducted in 1995.[3,4,27] During these previous studies, ammonium nitrate (NH_4NO_3) was the most prevalent species in the fine PM fraction in the SJV during wintertime stagnation events. NH_4NO_3 is not emitted directly (primary PM) but rather it forms through the condensation of gas-phase ammonia (NH_3) and nitric acid (HNO_3; secondary PM) as follows: (1)

$$HNO_{3(g)} + NH_{3(g)} \leftrightarrow NH_4NO_{3(s)} \qquad (1)$$

The equilibrium between the phases illustrated by eq 1 is both temperature- and relative humidity (RH)-dependent but favors the particle phase under typical wintertime conditions in the SJV. Gaseous HNO_3 has been found to constitute only 10–20% of total nitrate (NO_3^-) during winter months because of the low wintertime temperatures and the abundance of NH_3. Particle NH_4NO_3 concentrations have been found at similar levels at widely separated monitoring sites in the SJV, suggesting valley-wide mixing to combine the NH_3 released from large rural sources with HNO_3 formed from oxides of nitrogen (NO_x) released in urban areas.[25]

Very little is known currently about the composition, spatial, and temporal distribution of $PM_{0.1}$ in the SJV.

One study described the mass concentration and composition of $PM_{0.1}$ at Bakersfield,[28] while a second study measured particle number distributions at Fresno[7] (with no composition information reported).

SAMPLING LOCATIONS

Samples were collected at Bodega Bay, Davis/Sacramento, Modesto, Bakersfield, and Sequoia (Figure 1). These five locations were chosen to best characterize the spatial distribution of PM in the SJV and to allow for later modeling of the data. The Davis/Sacramento, Modesto, and Bakersfield sites were urban locations designed to characterize airborne PM from north to south in the SJV. The Bodega Bay and Sequoia sites were designed to characterize background concentrations outside the SJV. Table 1 contains the latitude, longitude, and elevation of each sampling location. A brief description of each sampling location is provided here.

Bakersfield is located at the southern end of the SJV. It is surrounded on three sides by mountains that rise to 1500 m in the south and east and 760 m in the west. Southeast of Bakersfield, the Tehachapi pass (1225 m) connects the SJV to the Mojave Desert. South of Bakersfield, the Tejon Pass (1250 m) leads to the South Coast Air Basin surrounding Los Angeles. Samples were collected in Bakersfield at 5558 California Avenue, in a low-density mixed residential/commercial area on the roof of a single-story office building. An oil refinery and a major highway (State Route 99) are both within 2 km of the site.

Modesto is located ~320 km north-northwest of Bakersfield in the northern end of the SJV halfway between the Coastal and Sierra Mountains. The Coastal Mountains in this part of the valley have nominal elevations of 500 m, although Mt. Diablo directly west of Modesto reaches 1173 m. The Sierra Nevada Mountains east of Modesto rise to 3000 m with individual peaks exceeding 4300 m. The Carquinez Straight and the Altamont Pass (elevation 304 m) northwest of Modesto connect the SJV to the San Francisco Bay area. Samples were collected in Modesto at 814 14th Street in a mixed residential/commercial area, less than 1km from a major

Table 1. Location of sampling sites.

Site name	Latitude ±2″	Longitude ±2″	Elevation ±1 m
Bakersfield	N 35° 21′ 24″	W 119° 3′ 45″	119
Bodega Bay	N 38° 19′ 8″	W 123° 4′ 22″	17
Davis	N 38° 32′ 11″	W 121° 45′ 12″	30
Modesto	N 37° 38′ 31″	W 120° 59′ 40″	28
Sacramento	N 38° 36′ 49″	W 121° 22′ 5″	26
Sequoia	N 36° 29′ 22″	W 118° 49′ 45″	535

highway (State Route 99) on the roof of a single-story building.

Sacramento and Davis are located ~120 km north of Modesto in the southern part of the Sacramento Valley. Davis and Sacramento are treated as a single sampling site because they both serve to characterize airborne PM north of the SJV. Samples were collected in Sacramento during the two first sampling events in December 2000, and the Davis site was used during the last two sampling events in January–February 2001. The geography surrounding Sacramento and Davis is similar to the geography surrounding Modesto. Samples were collected in Sacramento at 2701 Avalon Drive on top of a trailer located in a strictly residential area within 3 km of Interstate 80 and 5 km of U.S. Highway 50. Samples were collected in Davis at the University of California at Davis (UC Davis) campus on the second-story balcony of the Civil and Environmental Engineering building. The campus is located within 1 km of residential areas, farms, Interstate 80 and California Highway 113.

Bodega Bay is a small coastal town located directly west of Sacramento ~100 km north of San Francisco. The site is useful for the characterization of airborne particles reaching the California landmass from the ocean. It is separated from the Central Valley by the Coastal Mountains. Samples were collected in Bodega Bay on the roof of the UC Davis Bodega Marine Laboratory within 20 m of the Pacific Ocean.

Sequoia National Park is located on the western slopes of the Sierra Nevada mountain range ~120 km northeast of Bakersfield. The mountains directly east of the sampling site reach elevations greater than 4000 m. Samples were collected at the Ash Mountain IMPROVE monitoring site. Vehicle traffic in the park during the winter season (when sampling took place) is minimal, so most of the PM at Sequoia is transported to the site from other locations. Elevation at the sampling site is 535 m above mean sea level (MSL).

METEOROLOGICAL TRENDS

Figure 2 shows the times of meteorological events during the study period. A strong stagnation event started on December 16, 2000, and lasted until January 7, 2001. During this event, typical nighttime temperatures at Bakersfield and Modesto were 0 °C, with a maximum of 4.8 °C measured at Bakersfield on December 16, 2000, and a minimum of −6.7 °C measured at Modesto on December 27, 2000. Temperatures at 850 mb averaged 12.6 °C during this time creating a strong temperature inversion that trapped pollutants close to the ground. A weak upper-level disturbance briefly broke down the ridge on December 24, after which it was quickly re-established. A series of storms traversed the region on January 8–12 and again on January 23–25, 2001, bringing rain that reduced airborne pollutant concentrations and effectively ended the air quality episode. A second weaker episode started to build on January 28 and lasted beyond the end of sampling on February 3, 2001. Nighttime temperatures during this second episode were ~2.5 and −1 °C at Bakersfield and Modesto, respectively, with temperatures at 850 mb between 4 and 6 °C.[29]
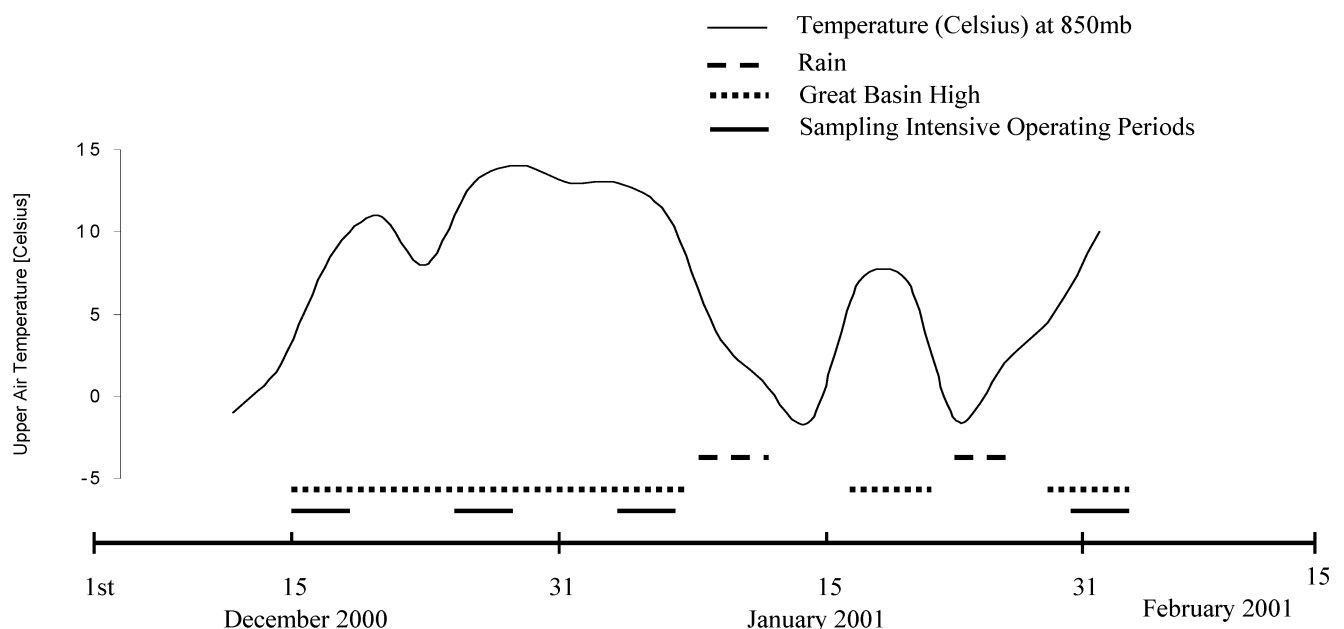

Figure 2. Meteorological patterns at Fresno and sampling schedule during the study period.

EXPERIMENTAL METHODS

Sampling took place during four separate Intensive Operating Periods (IOPs) from December 2000 through early February 2001 (Figure 2). IOP1 took place from December 15 to 18, 2000; IOP2 took place from December 26 to 28, 2000; IOP3 took place from January 4 to 7, 2001; and IOP4 took place from Jan 31 to February3, 2001 (all dates inclusive). Sample collection at all sites was started at 00:00 Pacific Standard Time (PST) on the first day of an IOP. At Bodega Bay, Davis, and Sequoia, one daily 22-hr sample was taken from 00:00–22:00, allowing 2 hr to unload and reload the samplers with new filters. At Bakersfield, Modesto, and Sacramento, one daytime sample was collected between 10:00 and 18:00 (8 hr duration) and one nighttime sample was collected between 20:00 and 08:00 the following morning (12 hr duration).

Samples were collected at each site using a filter-based sampler (RAAS2.5–400, Andersen Instruments, or equivalent) and two collocated Micro-Orifice Uniform Deposit Impactors (MOUDI model 110, MSP Corp.). At the Modesto site, a scanning mobility particle sizer (SMPS, TSI model 3936 L25) also was employed during IOP3. Filter-based samplers were configured to collect airborne PM (PM_{10} and $PM_{1.8}$) and gas-phase NH_3 and HNO_3. The PM_{10} sampling train included a PM_{10} inlet (Sierra Andersen 185) followed by Teflon (R2PJ047, Pall Corp.), quartz (QAO 47, Pall Corp.), and nylon (Nylasorb, Pall Corp.) filters operated in parallel. Nylon filters were coated with sodium carbonate ($NaCO_3$) to trap gaseous and particulate acid species. The $PM_{1.8}$ sampling train included an Air and Industrial Hygiene Laboratory (AIHL)-equivalent cyclone separator[30] operated at 30 L/min followed by four sampling legs. The first sample leg consisted of a Teflon filter (R2PJ047, Pall Corp.), followed by two glass fiber filters (Type A/E, Pall Corp.) coated with oxalic acid to trap gaseous NH_3. The back-up glass filter was used to guard against situations where breakthrough occurred on the front filter. In all cases, concentrations on the back-up filter were below detection, indicating that the front filter trapped all of the gas-phase NH_3. The second sample leg consisted of a Nylon filter coated with $NaCO_3$, while the third sample leg consisted of an annular denuder coated with MgO followed by a Nylon filter coated with $NaCO_3$. The difference in total NO_3^- concentration measured by sample legs two and three provides the concentration of gaseous HNO_3 via the denuder difference approach.[31] The fourth sample leg contained a quartz fiber filter (QAO 47, Pall Corp.) followed (in some cases) by backup quartz filters to identify adsorption artifacts. Quartz filters were baked at 550 °C for 48 hr before use to remove background carbon.

Two MOUDIs were used at each sampling location to support the full range of chemical analyses needed to characterize the size and composition distribution of airborne particulate matter. The first MOUDI was loaded with 47-mm foil substrates (MSP Corp.) and a 37-mm quartz after-filter (Pallflex 2500 QAO). The second MOUDI was loaded with 47-mm Teflon substrates (Teflo, R2PJ047) and a 37-mm Teflon after-filter (Zeflour, P5PJ037). Both MOUDIs were equipped with AIHL-design cyclone separators operated at 30 L/min to remove particles larger than 1.8 μm.[30]

Airflow in the filter samplers was controlled with critical orifices. Flow rates were measured either continuously during sampling or immediately before and after each sample event. Airflow in the MOUDIs was set to factory-recommended values and monitored continuously during sample collection. All flow measurements were accurate to within 5%.

All sample collection media were housed in sterile Petri dishes that were sealed with Teflon tape and stored in a freezer at −18 °C. Petri dishes used to hold foil and quartz filters were lined with aluminum foil that had been baked for 48 hr at 550 °C to prevent any carbon contamination. Sample collection media were transported to and from the collection sites in coolers kept at ~0 °C.

Aluminum substrates and Teflon filters were both preweighed and postweighed to determine gravimetric mass concentrations using a CAHN-33 microbalance (resolution of ±1 μg). The temperature and RH were monitored constantly during gravimetric analysis and were found in the range of 21–24 °C and 35–48%, respectively, and averaged 22 °C and 40%, respectively. Teflon filters were cut in half after postweights were collected. The first half of each Teflon filter was extracted in water and analyzed by ion chromatography (Dionex DX600) for the concentration of water-soluble ions [sodium (Na^+), calcium (Ca^{2+}), ammonium (NH_4^+), potassium (K^+), chloride (Cl^-), NO_3^-, sulfate (SO_4^{2-}), and phosphate (PO_4^{3-})]. The second half of each Teflon filter will be analyzed for insoluble metals. Coated nylon and glass fiber filters were extracted similarly and analyzed with ion chromatography for water-soluble NO_3^- and NH_4^+, respectively.

Aluminum and quartz filters were analyzed for total carbon, organic carbon, and EC using the NIOSH 5040 thermal optical transmittance method described by Birch and Cary.[32] In the current study, a factor of 1.4 was used to convert organic carbon measurements to OC measurements.[33] In the first stage of analysis, organic carbon is evolved in a helium (He) atmosphere as the temperature is stepwise increased to 870 °C. The evolved carbon is oxidized catalytically to carbon monoxide (CO_2) in a bed of granular manganese oxide (MnO_2) and then reduced to methane (CH_4) in a nickel/firebrick methanator. CH_4 is quantified with a flame-ionization detector (FID). In the second stage of analysis, the temperature is reduced, an

oxygen (O_2)-He mix is introduced, and the temperature is increased stepwise to 900 °C. Pyrolitically generated EC artifacts are corrected by monitoring the "blackness" of the sample (proportional to light absorption) using a laser transmittance technique. The transmittance decreases as pyrolitically generated EC is formed during the first stage of analysis. As O_2 enters the oven, pyrolytically generated carbon is oxidized, and a concurrent increase in filter transmittance occurs. The point at which the filter transmittance reaches its initial value is defined as the split between organic carbon and EC. The foil substrates loaded in MOUDIs are not translucent, and the split between organic carbon and EC cannot be determined using laser transmission. The fraction of organic carbon that evolves from collocated quartz filters in the O_2-He atmosphere is used to correct EC/organic carbon measurements made using MOUDI foil substrates.

Adsorption of gaseous OC onto quartz filters can cause positive biases in the determination of particle organic carbon.[34] To correct for this bias, the amount of carbon adsorbed on downstream quartz filters is subtracted from the upstream measurement. For locations where no backup quartz filter was used (Sacramento/Davis and Sequoia), the carbon concentrations were corrected for gas-phase adsorption by subtracting the average of the adsorbed fraction from the other sites (15%). Adsorption onto impactor substrates is negligible because of small effective surface area.

QUALITY CONTROL
Field Blanks
During the study, 10% of the filters transported to the sites during each IOP were designated as field blanks and later analyzed in the laboratory along with the collected ambient samples. The concentrations typically were close to or below the detection limit of the instrument (microbalance, IC, carbon analyzer). Whenever the average field blank concentrations were above instrument detection limits, they were subtracted from the ambient samples before ambient concentrations were calculated.

Uncertainty
Table 2 shows the average uncertainty and method detection limits associated with each chemical species quantified in the current study. The average uncertainty reflects possible error in the sample flow rate, fraction of filter analyzed, extraction fluid amount (for IC analysis), and analytical instrument result. The average uncertainty in instrument results was determined by analyzing the difference between original and duplicates run on every 10th sample. The average uncertainty in ambient concentration varies from a minimum of 7.1% for mass to a maximum 15.8% for Ca^{2+}. Because of the concentration-dependent instrument error, the actual uncertainty for each calculated ambient concentration reported is expected to be larger than the average uncertainty shown in Table 2 for low ambient concentrations and smaller than the average uncertainty shown in Table 2 for high ambient concentrations.

Data Consistency
The filter samplers located at Bodega Bay, Modesto, and Bakersfield collected duplicate samples on collocated Teflon filters that can be compared for gravimetric mass and water-soluble ions to provide an indication of data consistency. Figure 3a shows a scatter plot of these soluble

Table 2. Minimum detection limits for filter and MOUDI samples.

Species	Filter sample (ug m^{-3})			MOUDI sample (ug m^{-3})			Average uncertainty %
	8-hr Sample	12-hr Sample	22-hr Sample	8-hr Sample	12-hr Sample	22-hr Sample	
OC	0.33	0.22	0.12	0.11	0.07	0.04	8.7
EC	0.33	0.22	0.12	0.11	0.07	0.04	8.7
Chloride	0.03	0.02	0.01	0.01	0.01	0.01	14.1
Nitrate	0.01	0.01	0.01	0.01	0.01	0.01	12.6
Sulfate	0.04	0.02	0.01	0.01	0.01	0.01	13.2
Sodium	0.09	0.06	0.03	0.03	0.02	0.01	14.6
Ammonium	0.03	0.02	0.01	0.01	0.01	0.01	12.9
Potassium	0.02	0.01	0.01	0.01	0.01	0.01	13.6
Calcium	0.05	0.03	0.02	0.02	0.01	0.01	15.8
Gravimetric mass*	2.08	1.39	0.76	0.69	0.46	0.25	7.1
Reconstructed mass**	0.01	0.01	0.01	0.01	0.01	0.01	40

*Measured directly using micro balance.

**Sum of individual chemical species detected.

a

Collocated PM$_{1.8}$ Filter Measurements

b

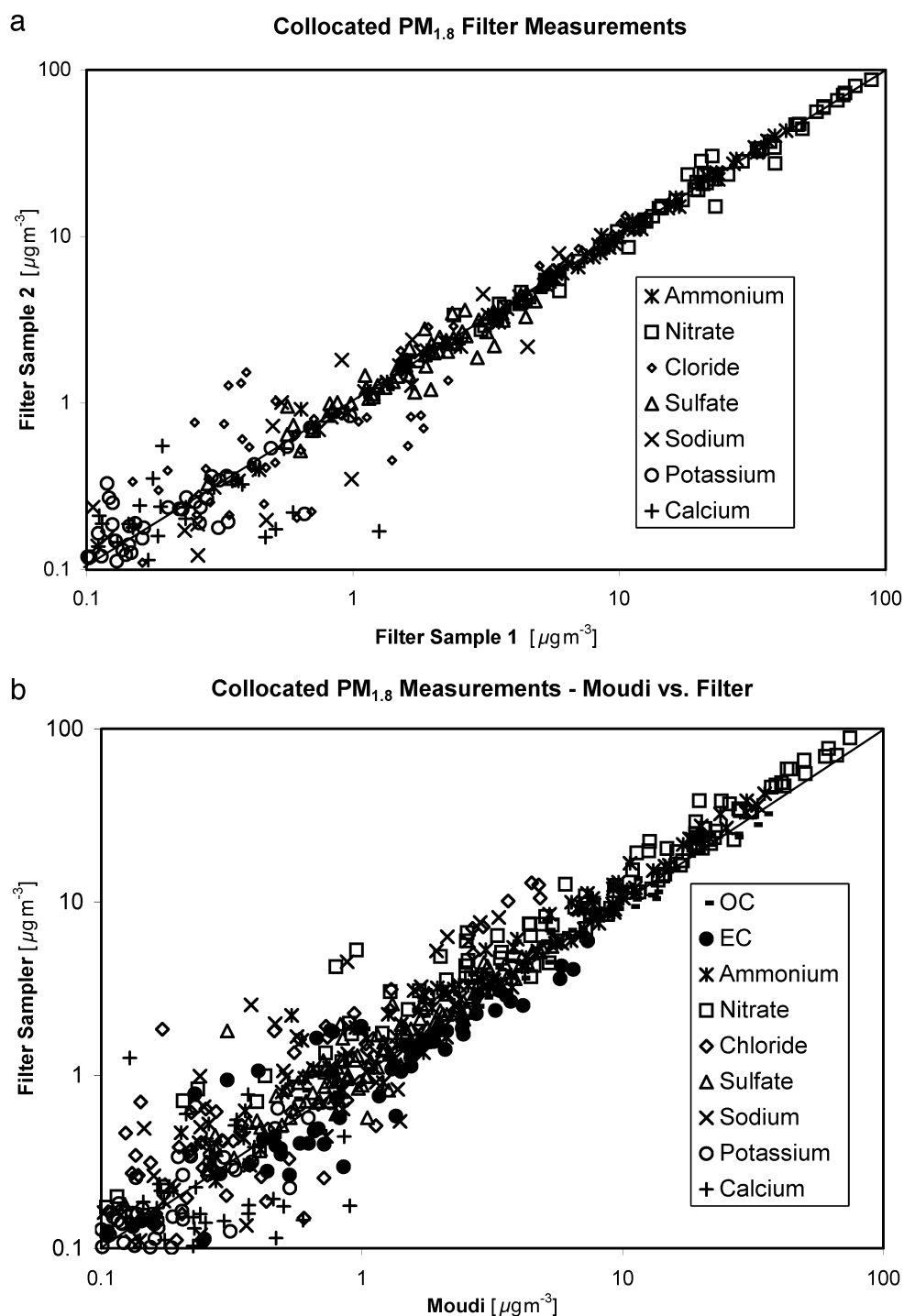**Collocated PM$_{1.8}$ Measurements - Moudi vs. Filter**

Figure 3. Comparison between (a) collocated filter samples and (b) filter samples vs. MOUDI samples collected at all sites during the study period.

ions. Agreement in the calculated ambient concentrations improves significantly when a species is found with some abundance, generally above 1 μg/m³. Species found at high concentration, such as mass, NO_3^-, and NH_4^+ have slopes very close to 1 and correlation coefficients greater than 0.98. Several of the species found at lower concentrations, such as SO_4^{2-}, Cl^-, and Na^+ have quite good agreement with correlation coefficient values greater than

0.85. Of the remaining species, K^+ has a correlation coefficient equal to 0.8, and Ca^{2+} has a correlation coefficient equal to 0.22. The ion chromatography unit used for cation analysis previously has been used to detect very high Ca^{2+} concentrations. Residual amounts of Ca^{2+} still in the instrument interfere with the accurate detection of trace amounts of Ca^{2+}, resulting in the very low correlation coefficient. Ca^{2+} for the current study

will be quantified using an inductively coupled plasma mass spectrometer and reported in a subsequent publication. PO_4^{3-} was not detected at any of the sites and has not been included in the analysis.

Another consistency check can be made by comparing collocated $PM_{1.8}$ samples collected using MOUDI and filter samplers for mass, water-soluble ions, and carbon. Figure 3b shows a scatter plot of filter-based versus MOUDI-based $PM_{1.8}$ ambient concentrations. As with the internal filter sampler comparison, agreement improves as ambient concentrations increase to above ~1 µg/m³. All species other than Na^+, K^+, and Ca^{2+} have correlation coefficients of 0.9 or greater.

RESULTS
Gravimetric

Figure 4 shows $PM_{0.1}$ particle mass measured with a SMPS and a MOUDI at Modesto during the period January 4–7, 2001 (IOP3). The SMPS counted particles in the size range 16–764 nm with a time resolution of 7.5 min. Particle number counts in the $PM_{0.1}$ size range were transformed to mass estimates using a density of 1.2 g/cm³. $PM_{0.1}$ mass measurements made with MOUDIs show strong agreement with SMPS measurements. SMPS $PM_{0.1}$ estimates are slightly greater than the gravimetric measurements, possibly because of the larger particle range included in the SMPS data (16–100 nm) versus stage 10 on the MOUDI (56–100 nm) and the uncertainty in the particle density.

The data show two distinct ultrafine events in any given 24-hr period. One event occurs in the evening between 6:00 p.m. and 11:00 p.m., while a second smaller event occurs in the morning before noon. The timing of these ultrafine events is consistent with increased combustion activities observed during the evening (home heating, traffic) and morning (traffic) hours.

Figures 5a-c show the concentration of $PM_{0.1}$, $PM_{1.8}$, and PM_{10} measured during the study period at Bakersfield, Bodega Bay, Sacramento, Davis, Modesto, and Sequoia. Peak $PM_{0.1}$ concentrations were 2.3 ± 0.3 µg/m³ at Sacramento on the evening of December 28, 2000, and 2.4 ± 0.3 µg/m³ at Bakersfield on the evening of February 1, 2001. Nighttime concentrations of $PM_{0.1}$ at Bakersfield, Modesto, and Sacramento were typically 1–2 µg/m³. These concentrations are comparable to the average $PM_{0.1}$ concentrations of ~1.5 µg/m³ inferred by conversion of the particle number distribution reported by Watson et al.[7] at Fresno. $PM_{0.1}$ concentrations were low at the remaining sites and did not vary significantly during each IOP. At Davis, concentrations ranged from a minimum of 0.33 µg/m³ to a maximum of 0.56 µg/m³. At Sequoia, six out of the 15 samples collected showed no detectable $PM_{0.1}$ mass, and average concentration was only 0.07 µg/m³. At Bodega Bay, a single maximum $PM_{0.1}$ concentration of 1 µg/m³ was recorded on the first day of IOP1, with the remaining samples all showing $PM_{0.1}$ concentrations lower than 0.5 µg/m³ and averaging 0.2 µg/m³.
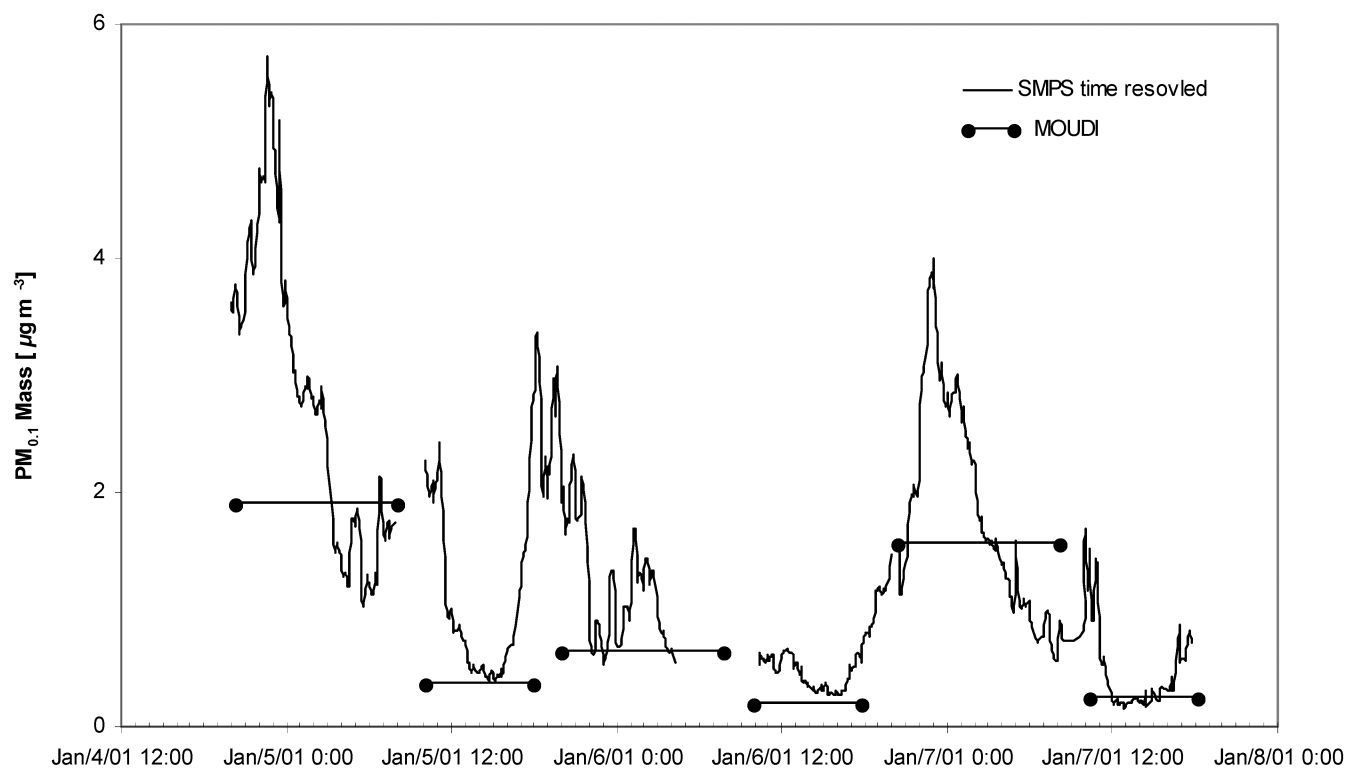

Figure 4. $PM_{0.1}$ mass at Modesto during IOP3. Particles were assumed to be spherical with a density of 1.2 g/cm³.
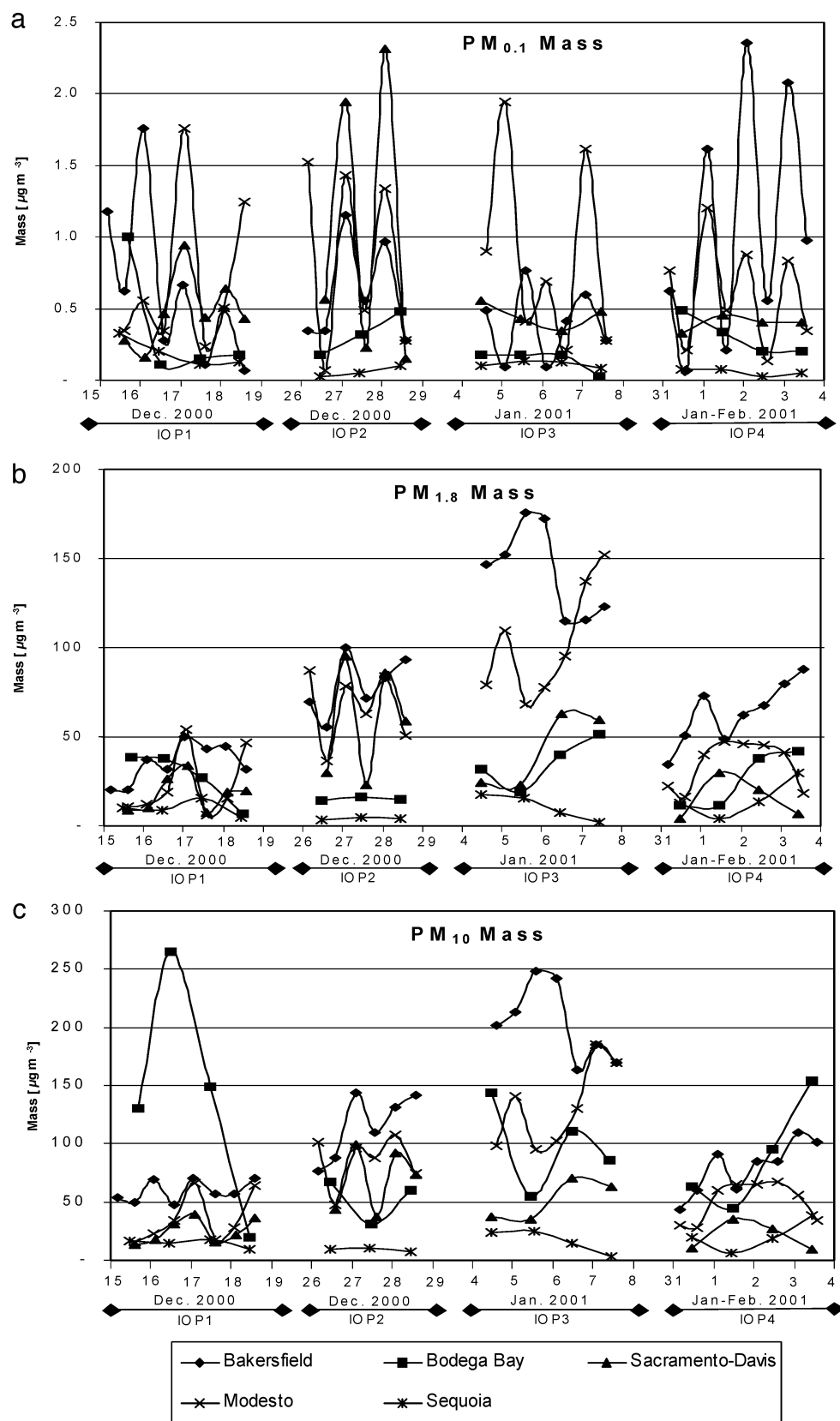
Figure 5. Variation of airborne particle mass concentrations during the study period. Reconstructed mass is used when gravimetric measurements fell below method detection limits.

$PM_{0.1}$ concentrations follow a strong diurnal pattern at all sites where both night and day samples were collected. Nighttime concentrations typically are more than double corresponding daytime concentrations. This trend likely results from lower atmospheric mixing depths at night combined with increased fuel combustion for home heating. Over longer time scales, $PM_{0.1}$ concentrations generally decrease at Bakersfield between December 15, 2000, and January 7, 2001. $PM_{0.1}$ concentrations at other sampling locations do not exhibit any significant long-term trend. This suggests that $PM_{0.1}$ has an atmospheric lifetime less than 24 hr and that $PM_{0.1}$ concentrations are driven locally by mixing depth and emissions.

Figure 5 shows that $PM_{1.8}$ mass steadily increases during IOPs 1–3 at the Modesto and Bakersfield sampling locations. The $PM_{1.8}$ concentration at Bakersfield started at 20 $\mu g/m^3$ on December 15, 2000, and peaked at 172 $\mu g/m^3$ on the evening of January 5, 2001. A similar trend is observed at Modesto, with an initial $PM_{1.8}$ concentration of 11 $\mu g/m^3$ on December 15, 2000, and a peak concentration of 152 $\mu g/m^3$ on January 7, 2001. The timing of the peak values suggests that the first stagnation event starts to break up in the southern end of the SJV. During the second stagnation event (IOP4), the initial $PM_{1.8}$ concentration at Bakersfield is 34 $\mu g/m^3$, with an increase to 89 $\mu g/m^3$ during the day of February 3, 2001. At Modesto, the $PM_{1.8}$ concentration starts at 22 $\mu g/m^3$ on January 31, 2001, increasing to 40–50 $\mu g/m^3$, and then decreasing to 18 $\mu g/m^3$ on February 3, 2001. $PM_{1.8}$ concentrations at Sequoia started at 10 $\mu g/m^3$ on December 15, 2000, and decreased to 4 $\mu g/m^3$ on December 18, 2000, where they remained through all of IOP2. During IOP3, $PM_{1.8}$ concentrations at Sequoia started at 18 $\mu g/m^3$ and steadily declined to 2 $\mu g/m^3$ by January 7, 2001. As shown in Table 1, Sequoia is located between Modesto and Bakersfield on the fringe of the eastern side of the SJV at an elevation of 535 m above MSL. Atmospheric mixing depths during IOP1–IOP3 were generally lower than this elevation, effectively isolating Sequoia from events on the valley floor. During IOP4, the trend in $PM_{1.8}$ concentration at Sequoia more closely resembled that of Bakersfield, suggesting that the site was not as isolated from the valley floor as during the first stagnation event. $PM_{1.8}$ during IOP4 increased from 13 to 30 $\mu g\ m^3$ (the maximum recorded at the site). $PM_{1.8}$ concentrations measured in Sacramento increase from 9 $\mu g/m^3$ on December 15, 2000, to 59 $\mu g/m^3$ on December 28, 2000. Strong diurnal variations in $PM_{1.8}$ concentrations were observed because of very high levels of woodsmoke through the Christmas holiday as seen on the night sample of December 26 and December 27, 2000. $PM_{1.8}$ concentrations at Davis were only 25 $\mu g/m^3$ at the beginning of IOP3 but increased to 59 $\mu g/m^3$ by January 7, 2001.

$PM_{1.8}$ concentration trends at Sacramento, Davis, and Modesto were similar, with concentrations in Sacramento comparable to Modesto and concentrations in Davis significantly lower. $PM_{1.8}$ concentrations measured at Bodega Bay had little in common with concentrations measured at the four other sites. During IOP1, $PM_{1.8}$ concentrations decreased steadily at Bodega Bay from an initial concentration of 39 $\mu g/m^3$ to a final concentration of 7 $\mu g/m^3$. During IOP2, $PM_{1.8}$ concentrations at Bodega Bay were constant at ~15 $\mu g/m^3$. During both IOP3 and IOP4, $PM_{1.8}$ concentrations increased at Bodega Bay in a fashion similar to trends observed at Davis and Modesto. $PM_{1.8}$ concentrations at Bodega Bay increased from 32 to 51 $\mu g/m^3$ during IOP3 and increased from 12 to 42 $\mu g/m^3$ during IOP4. The peak in the airborne particle mass distribution was at an aerodynamic diameter between 0.56 and 1 μm at all the sampling locations.

Figure 5c shows that PM_{10} and $PM_{1.8}$ concentrations and trends in the SJV are very similar during the present study. During the winter months, low wind speeds and moist soil from frequent precipitation suppresses the suspension of agricultural dust, a major contributor to the coarse PM fraction in the SJV during the fall months. PM_{10} concentrations at Bodega Bay were much larger than $PM_{1.8}$ concentrations, with different trends over time. This holds during IOP1 in particular when PM_{10} concentrations at Bodega Bay were measured in excess of 250 $\mu g/m^3$, while corresponding $PM_{1.8}$ concentrations were never above 50 $\mu g/m^3$. The increase in PM_{10} concentrations at the coastal site presumably is associated with production of sea spray aerosol during moderate wind speed events.

Chemical Components

Figure 6 shows the relative size distribution of airborne particle chemical composition at Bakersfield on December 26, 2000, as measured using cascade impactors. This particular sample was chosen because it represents the typical chemical size distribution in wintertime SJV atmospheric aerosol. The amount of each chemical component found in each size fraction is normalized by the aggregate amount of all species found in that size range. NH_4NO_3 dominated $PM_{1.8}$ and was found to peak just below 1 μm aerodynamic diameter. Below 0.32 μm, NH_4NO_3 contributed little to airborne particle mass. Carbon (both OC and EC) is an important contributor in all size fractions but completely dominates below 0.18 μm, where OC and EC combined typically constitute as much as 90% of the mass found.

Figure 7.1 shows the variation of $PM_{0.1}$ airborne particle chemical component concentrations at Bakersfield, Modesto, Sacramento-Davis, Bodega Bay, and Sequoia. OC and EC are the dominant chemical components in
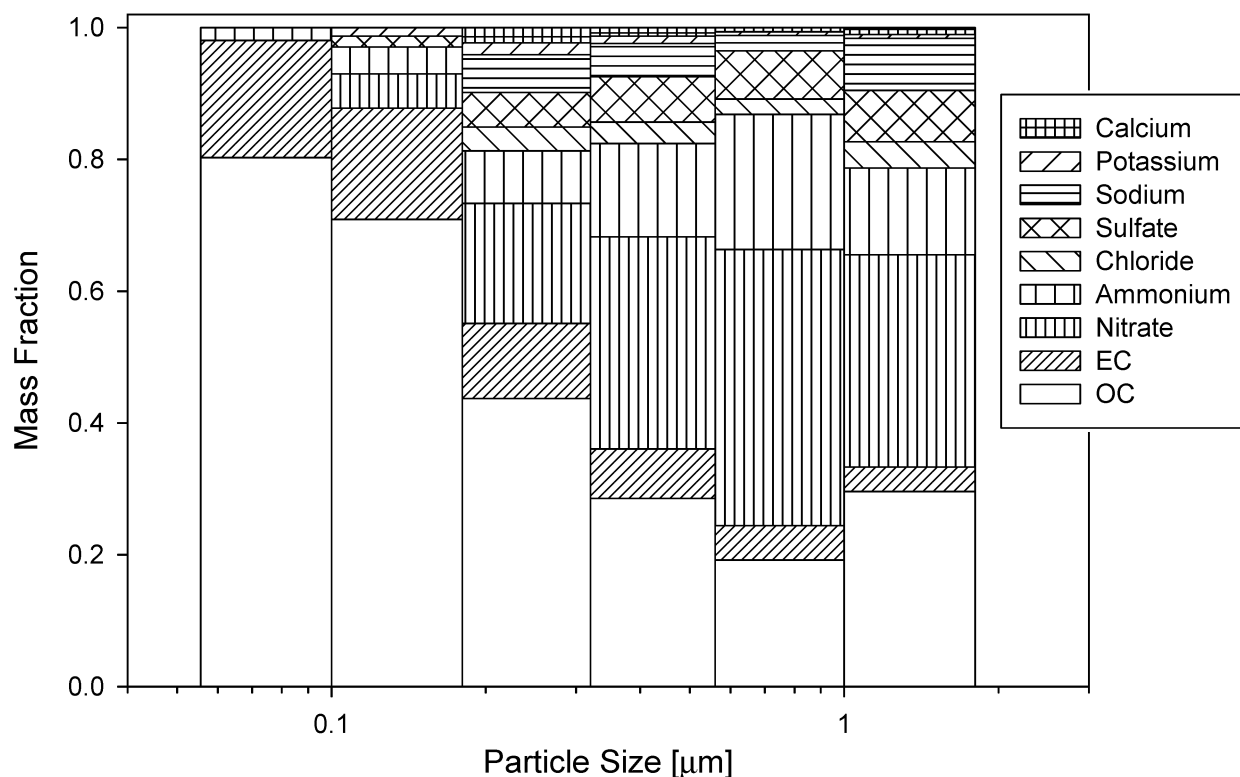
Figure 6. Relative size distribution of airborne particulate OC, EC, NH_4^+, NO_3^-, Cl^-, SO_4^{2-}, Na^+, K^+, and Ca^{2+} ions measured at Bakersfield on the evening of December 26, 2000. Results are typical of size distribution measured throughout the SJV during the study period.

the $PM_{0.1}$ size fraction at all locations on the floor of the SJV (Bakersfield, Modesto, Sacramento), accounting for 75 and 15% of the total mass on average. A distinct diurnal trend is evident at these locations: nighttime concentrations of OC and EC are a factor of 2–3 times larger than daytime concentrations. Over larger time scales, $PM_{0.1}$ concentrations of carbonaceous material at Bakersfield decrease between December 15, 2000, and January 7, 2001 (the period when $PM_{1.8}$ mass concentrations are peaking). $PM_{0.1}$ OC and EC concentrations at Bodega Bay and Sequoia are an order of magnitude lower than concentrations at the SJV sites. The presence of a diurnal trend could not be detected at these sites because 22-hr average samples were collected. Minor chemical components found in the $PM_{0.1}$ range include Ca^{2+}, Na^+, K^+, SO_4^{2-}, NO_3^-, and Cl^-. These species typically account for less than 10% of the $PM_{0.1}$ particle mass. The concentration of these species in the $PM_{0.1}$ size range typically was less than 0.5 $\mu g/m^3$ at all sampling locations, with clear diurnal patterns evident at Bakersfield and Modesto.

Figure 7.2 shows the variation of $PM_{1.8}$ airborne particle chemical component concentrations at Bakersfield, Modesto, Sacramento-Davis, Bodega Bay, and Sequoia. At

Bakersfield, Modesto, and Sacramento-Davis, wintertime fine PM is dominated by NH_4NO_3 and to a lesser extent by OC. NH_4NO_3 and OC typically constitute more than 75% of total $PM_{1.8}$ at these three sites. During very high particulate events (such as during IOP3), NH_4^+, NO_3^-, and OC constitute more than 90% of total $PM_{1.8}$ mass. NH_4NO_3 alone constituted 25–75% of total $PM_{1.8}$ mass, with higher fractions in the southern end of the SJV at Bakersfield. $PM_{1.8}$ NH_4NO_3 concentrations were weakly diurnal, with slightly greater concentrations observed during the day. The degree to which NH_4NO_3 was diurnal increased further south in the SJV but was not seen to be a function of concentration. $PM_{1.8}$ OC and EC concentrations were highly diurnal with greater values observed at night. Cl^- and K^+ were detected in relatively small amounts in the $PM_{1.8}$ size fraction in the SJV with concentrations of no more than 2 and 1 $\mu g/m^3$, respectively. The diurnal pattern of these ions was similar to that of OC and EC, suggesting that they are released from the same source, possibly woodsmoke.[35] SO_4^{2-} and Ca^{2+} concentrations at Bakersfield, Modesto, and Sacramento-Davis were less than 6 and 1 $\mu g/m^3$, respectively. No clear diurnal trend in the concentrations of these two ions was

Figure 7.1. Variation of $PM_{0.1}$ airborne particle chemical component concentrations during the study period. Two concentration ranges are used for each sampling site to illustrate the trends for major and minor components. Night (N) and day (D) samples are noted on the time axis at those locations where two daily samples were collected. All concentrations are in $\mu g/m^3$.
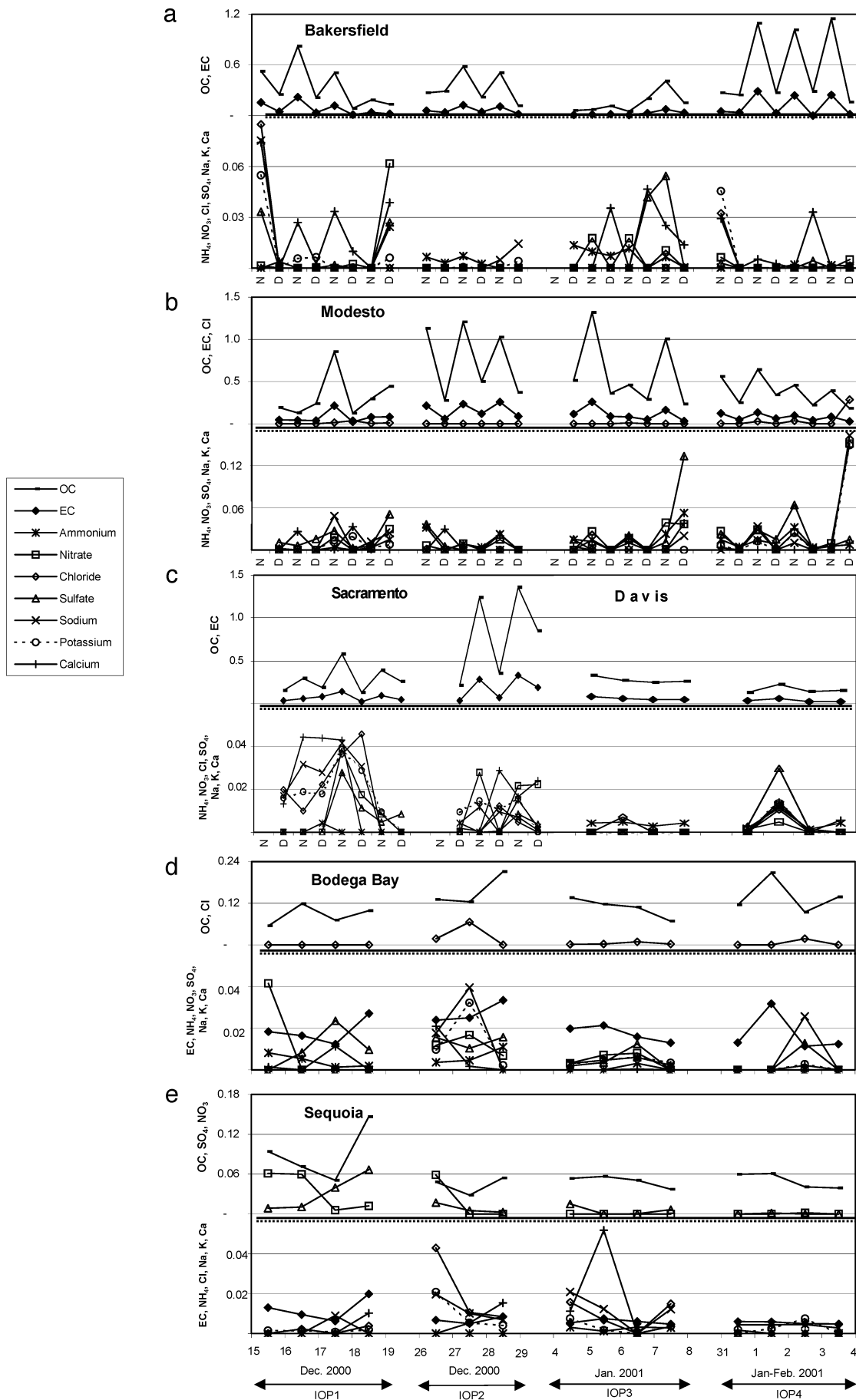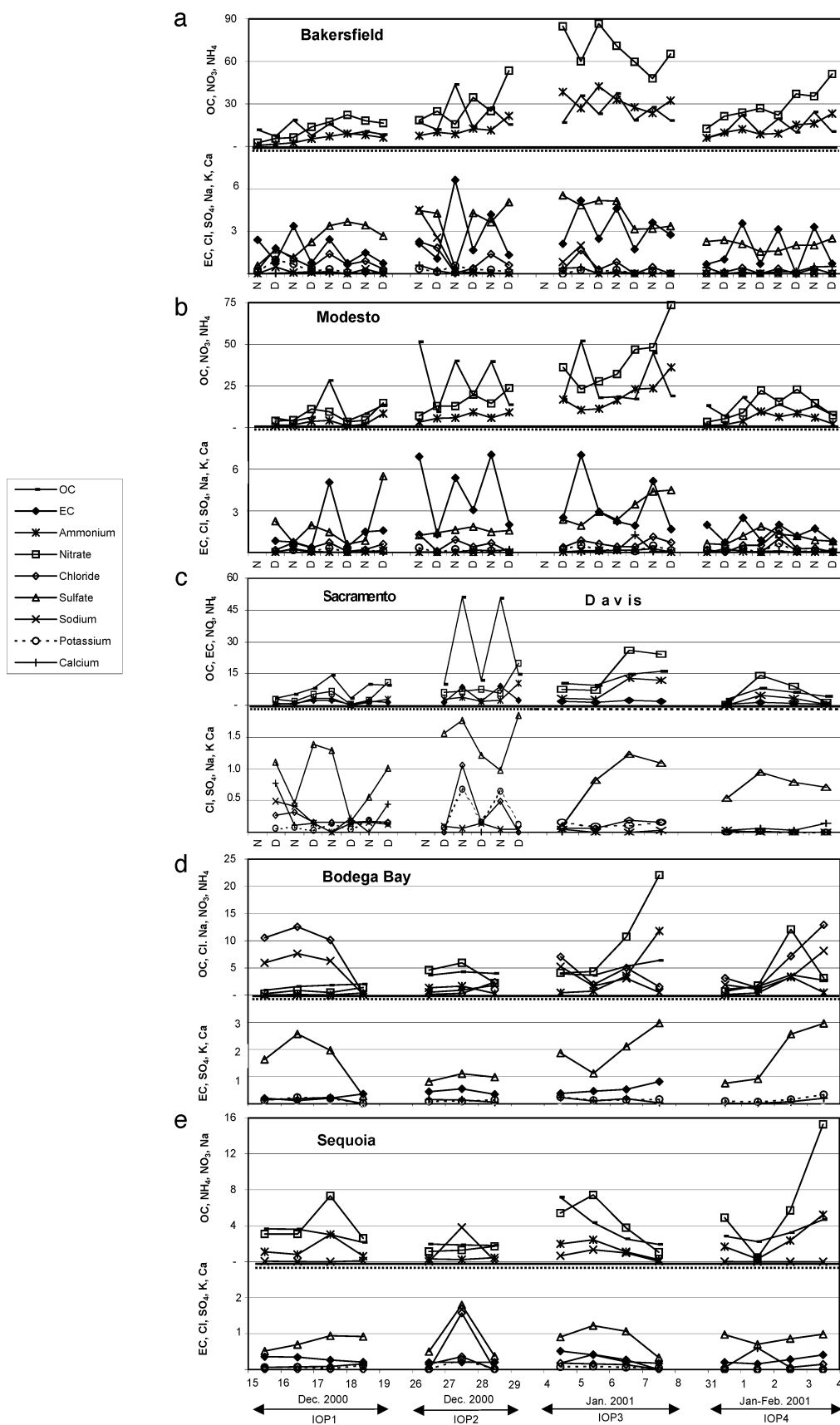
Figure 7.2. Variation of PM$_{1.8}$ airborne particle chemical component concentrations during the study period. Two concentration ranges are used for each sampling site to illustrate the trends for major and minor components. Night (N) and day (D) samples are noted on the time axis at those locations where two daily samples were collected. All concentrations are in μg/m^3.
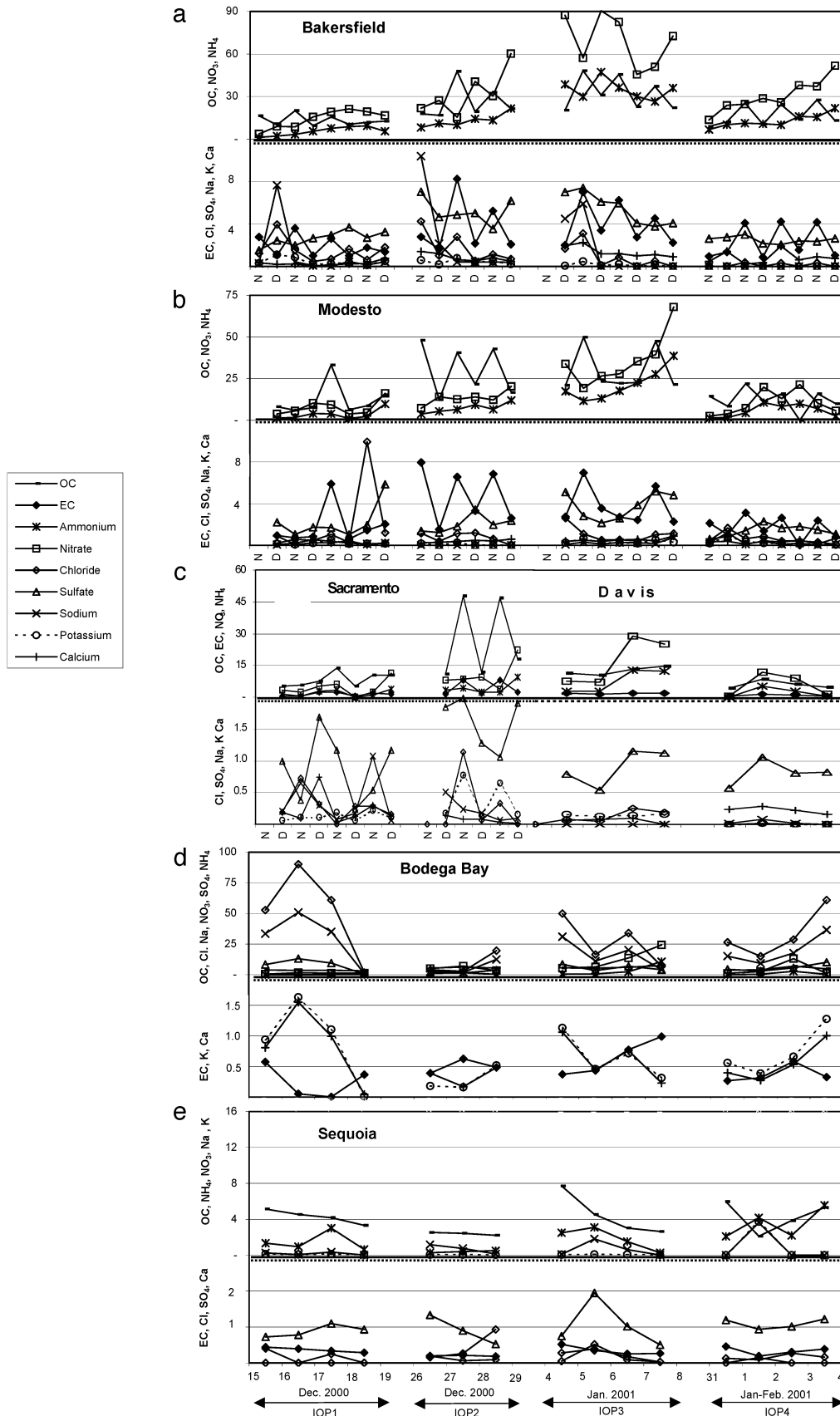
a

Bakersfield

b

Modesto

OC
EC
Ammonium
Nitrate
Chloride
Sulfate
Sodium
Potassium
Calcium

c

Sacramento　　　　D a v i s

d

Bodega Bay

e

Sequoia

| 15 | 16 | 17 | 18 | 19 | 26 | 27 | 28 | 29 | 4 | 5 | 6 | 7 | 8 | 31 | 1 | 2 | 3 | 4 |

Dec. 2000　　　Dec. 2000　　　Jan. 2001　　　Jan-Feb. 2001

IOP1　　　IOP2　　　IOP3　　　IOP4

Figure 7.3. Variation of PM$_{10}$ airborne particle chemical component concentrations during the study period. Two concentration ranges are used for each sampling site to illustrate the trends for major and minor components. Night (N) and day (D) samples are noted on the time axis at those locations where two daily samples were collected. All concentrations are in μg/m^3.

detected. $PM_{1.8}$ SO_4^{2-} concentrations at Bakersfield were slightly greater than background concentrations measured at Bodega Bay, suggesting a source in Kern County. $PM_{1.8}$ Na^+ concentrations measured during the study were less than 0.5 $\mu g/m^3$ at all times, with the exception of the samples collected at Bakersfield on December 26, 2000. The brief upper-level disturbance on December 24 brought some ocean air over the southern coastal mountains and into the southern SJV, resulting in $PM_{1.8}$ Na^+ concentrations of 4.5 and 2.5 $\mu g/m^3$ on that date.

OC and NH_4NO_3 typically constituted the majority (~80%) of $PM_{1.8}$ mass at the Sequoia sampling site. Concentrations were significantly lower than on the Valley floor, with NO_3^- reaching a maximum concentration in December of 7.5 $\mu g/m^3$ (vs. 87 $\mu g/m^3$ at Bakersfield) and NH_4^+ reaching a maximum concentration of 3 $\mu g/m^3$ (vs. 42 $\mu g/m^3$ at Bakersfield). Concentrations of other $PM_{1.8}$ species were low and steady during the sampling period, except for Na^+, Cl^-, and SO_4^{2-}, which reach their maximum values on December 27, 2000, when ocean air from the earlier upper-level disturbance is believed to have reached Sequoia. During the first and stronger episode (IOP1–IOP3), Sequoia was isolated from the shallow valley mixing layer, but during the second weaker episode (IOP4), atmospheric mixing depth was higher and $PM_{1.8}$ measurements at Sequoia followed the same trend as those on the valley floor. At the end of IOP4, $PM_{1.8}$ NH_4^+ and NO_3^- concentrations increased to values of 5 and 15 $\mu g/m^3$, respectively (20–30% of the values at Bakersfield).

The behavior of $PM_{1.8}$ concentrations at the coastal Bodega Bay sampling site was very different than the behavior observed in the SJV. $PM_{1.8}$ concentrations measured at Bodega Bay were generally low (less than 50 $\mu g/m^3$) and their constituents varied greatly over time. During the first three days of IOP1, traditional sea salt components (Na^+, Cl^-, SO_4^{2-}) make up 50–70% of total $PM_{1.8}$. On the fourth day of IOP1, Na^+, Cl^-, and SO_4^{2-} concentrations decline dramatically, as does $PM_{1.8}$ mass, while other constituents measured stay relatively constant. During IOP3, as the Great Basin High is breaking up, $PM_{1.8}$ concentrations at Bodega Bay become dominated by NH_4^+, NO_3^-, and OC. On January 4, 2001, NH_4NO_3 and carbon account for 23% of $PM_{1.8}$ mass at Bodega Bay, but this increases to 75% by January 7, 2001. $PM_{1.8}$ SO_4^{2-} concentrations increase in concert with NH_4^+ and NO_3^-, while Na^+ and Cl^- concentrations remain low. SO_4^{2-} during IOP3 is, therefore, more likely to originate with the NH_4^+ and NO_3^- transported to Bodega Bay than from sea salt. $PM_{1.8}$ concentrations at Bodega Bay during IOP4 are dominated by sea salt, leading to an increase in $PM_{1.8}$ levels. On the third day of IOP4, NO_3^- and NH_4^+ show uncharacteristically high concentrations during a period dominated by sea salt, but they decrease again the following day.

Figure 7.3 shows the variation of PM_{10} airborne particle chemical component concentrations at Bakersfield, Modesto, Sacramento-Davis, Bodega Bay, and Sequoia. Concentrations and trends are similar to those of $PM_{1.8}$ except for at Bodega Bay, where concentrations of Na^+, Cl^-, and SO_4^{2-} were much greater during the onset of IOPs 1 and 3 and at the end of IOP4.

Gas-Phase Results

Figure 8 shows the variation of gas-phase NH_3 and HNO_3 concentrations measured at Bakersfield, Bodega Bay, Sacramento-Davis, Modesto, and Sequoia during the study period. Gas-phase NH_3 follows the same pattern exhibited by $PM_{1.8}$ and other individual PM species during the first stagnation event (IOP1–IOP3). NH_3 concentrations increase as the stagnation event unfolds with SJV concentrations higher than Sacramento Valley concentrations. Peak concentrations measured at Bakersfield and Modesto were 34 and 62 $\mu g,m^3$, respectively. NH_3 concentrations at Bodega Bay, Sacramento-Davis, and Sequoia were relatively low during this time, with typical values less than 10 $\mu g/m^3$. During IOP4, there is no clear trend in the NH_3 concentration at the three sites in the Central Valley. The concentrations measured in Bakersfield and Modesto are in the 10–30 $\mu g/m^3$ range and at Davis in the 3–10 $\mu g/m^3$ range. Gas-phase NH_3 is always present in relatively large concentrations in the SJV (Modesto and Bakersfield) but gas-phase NH_3 concentrations at Bodega Bay and Sequoia are low throughout the sampling period. This strongly suggests the presence of significant NH_3 sources in the SJV.[1,25]

Gas-phase HNO_3 concentrations were much lower than NH_3 concentrations throughout the study period. HNO_3 concentrations were below detection limits in 28% of all measurements taken and less than 1 $\mu g/m^3$ in 77% of all measurements. In general, the only significant concentrations occurred as singular events. Spikes of higher concentrations were recorded at Sacramento with 4 $\mu g/m^3$ during IOP1 and 4 and 8 $\mu g/m^3$ both during IOP2. Spikes in HNO_3 concentrations were also observed at Bakersfield with 5 and 7 $\mu g/m^3$ during IOP2 and IOP3, respectively, and at Modesto with 3 and 4 $\mu g/m^3$ both during IOP3. Spikes in HNO_3 concentrations did not follow a repeatable diurnal pattern. These measurements show that the vast majority of NO_3^- is contained in the particle phase and that NH_4NO_3 aerosol formation is limited by the availability of HNO_3.

Principal Component Analysis

Principal component analysis (PCA) is a useful technique for the identification of relationships between variables in a complex data set. PCA quantifies the temporal variation of each variable in the data set about its mean value and
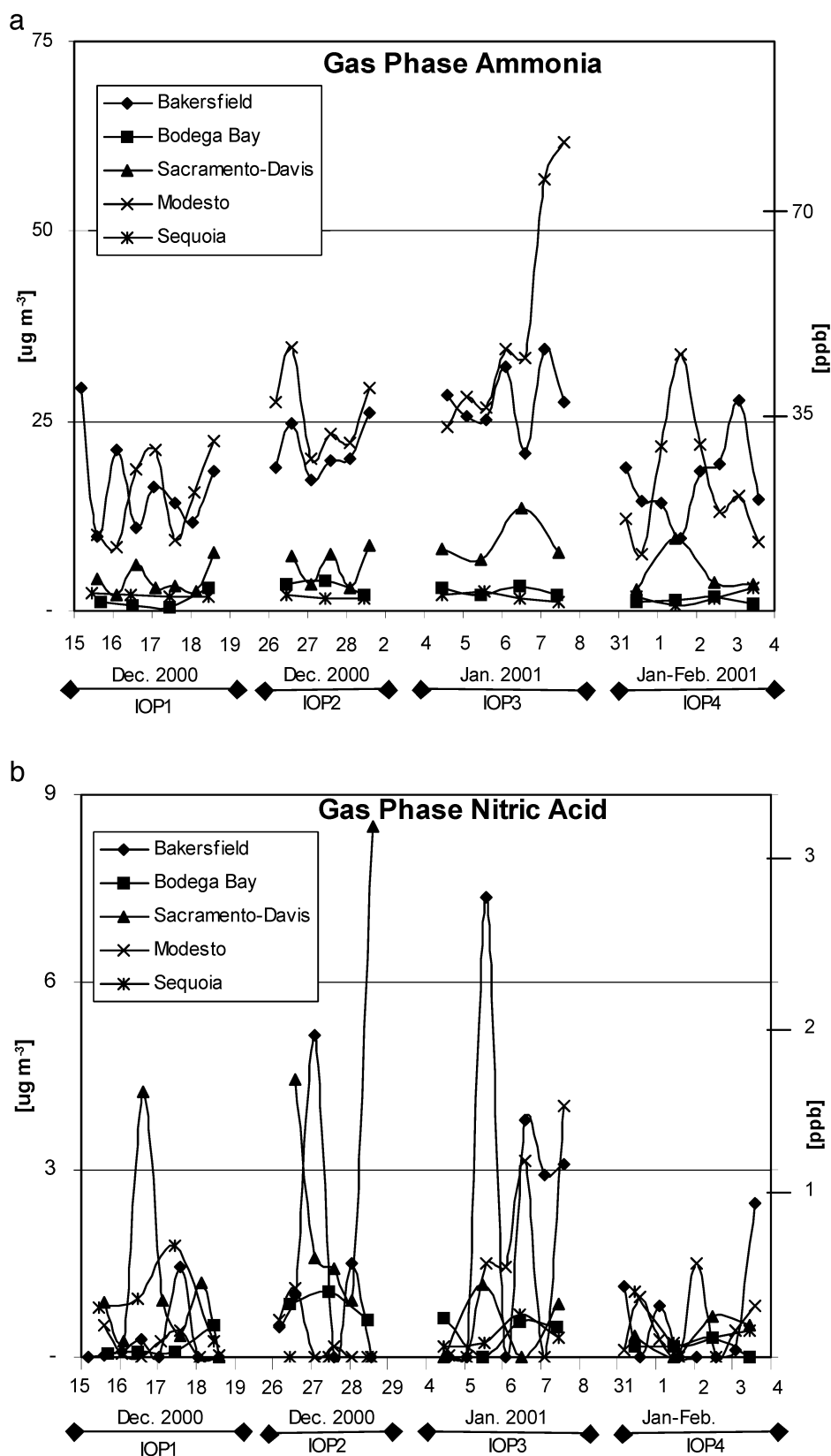
a

b

Figure 8. Variation of gas-phase NH_3 and HNO_3 concentrations during the study period.

groups variables with similar behavior together into principal component (PC) directions. Each PC identified by the method is uncorrelated from other PCs, and the PCs

that explain the majority of the total variation in the entire data set are identified first. It should be noted that the PCs identified in an air-quality data set are not directly

equivalent to source signatures. The identification of source signatures using statistical methods is a complex task requiring advanced methods.[36] In the present study, PCA will be used to identify obvious relationships between particle components that suggest broad source categories.

Figures 9-11 show the PCs of the data matrices for $PM_{0.1}$, $PM_{1.8}$, and coarse PM (PM_{10}–$PM_{1.8}$) at Bakersfield, Bodega Bay, Sacramento, Davis, Modesto, and Sequoia. Only PCs that explain more than 5% of the variance are shown. The PCs for the ultrafine fraction (Figure 9) show $PM_{0.1}$ on the valley floor to be completely dominated by OC and EC, suggesting a combustion source. PC1 accounts for 95% or more of total variance in the data set for

Bakersfield, Modesto, Sacramento, and Davis. At Sequoia, NO_3^- and SO_4^{2-} also appear in PC1, which only accounts for 53% of the variance. A second PC for Sequoia, representing 26% of variance, is composed of Na^+, Cl^-, and NO_3^-. This suggests various sources for the $PM_{0.1}$ fraction at Sequoia, with possible contributions from aged combustion particles and reacted sea-salt aerosol. At Bodega Bay, PC1 is dominated by OC and EC, accounting for 73% of the variance. A second PC at Bodega Bay, accounting for 19% of variance, consists of Na^+, Cl^- and, to a lesser extent, K^+. This chemical signature suggests fresh sea-salt aerosol.

The first two PCs for $PM_{1.8}$ (Figure 10) account for more than 95% of total variance in all cases and account
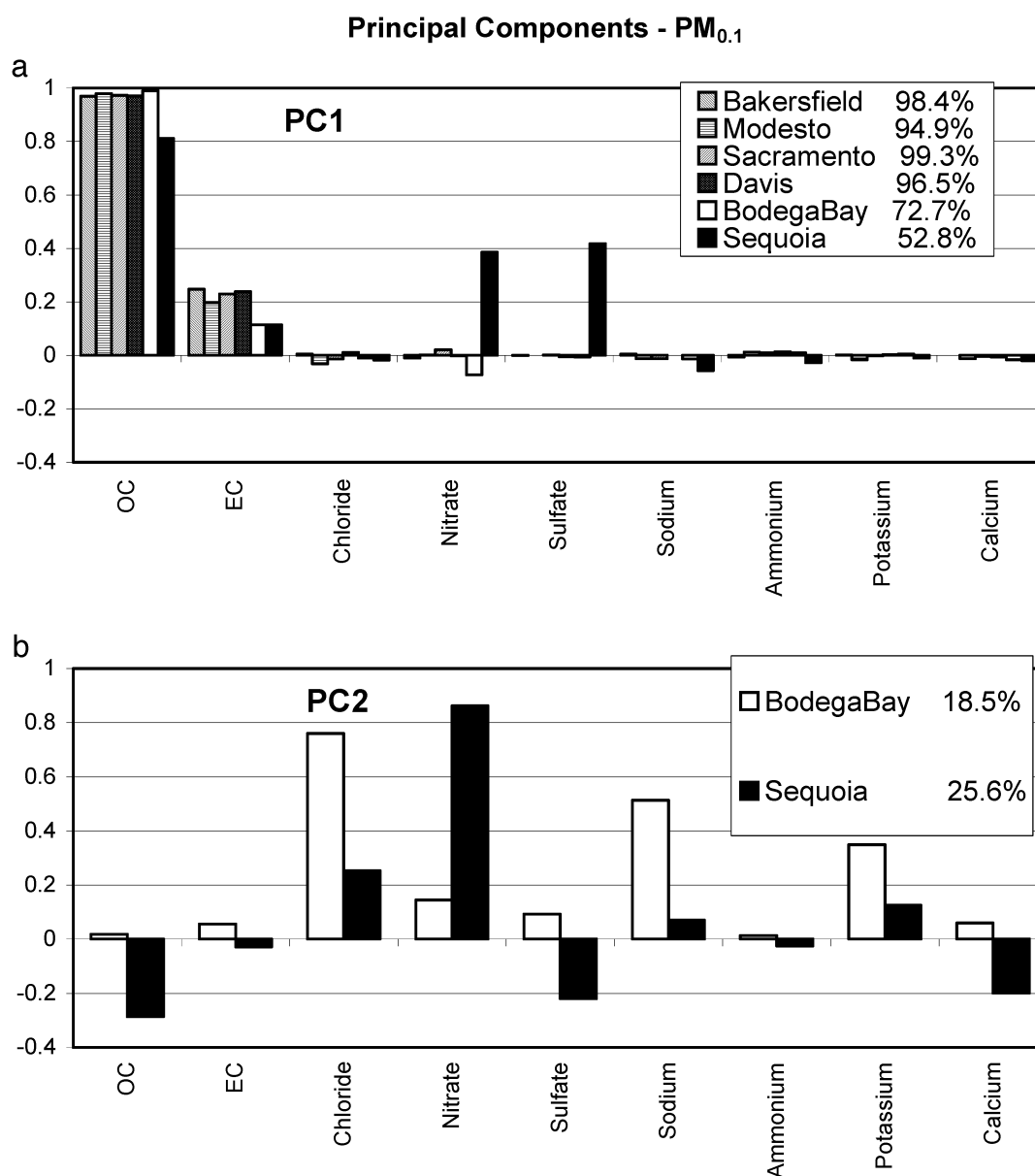
Principal Components - $PM_{0.1}$

Figure 9. PCA of $PM_{0.1}$ concentrations at Bakersfield, Bodega Bay, Davis, Modesto, Sacramento, and Sequoia. The percentage of variance explained by each PC is shown in the key adjacent to the sampling location. The second PC is shown for Bodega Bay and Sequoia to explain significant residual variance not covered by the first PC.
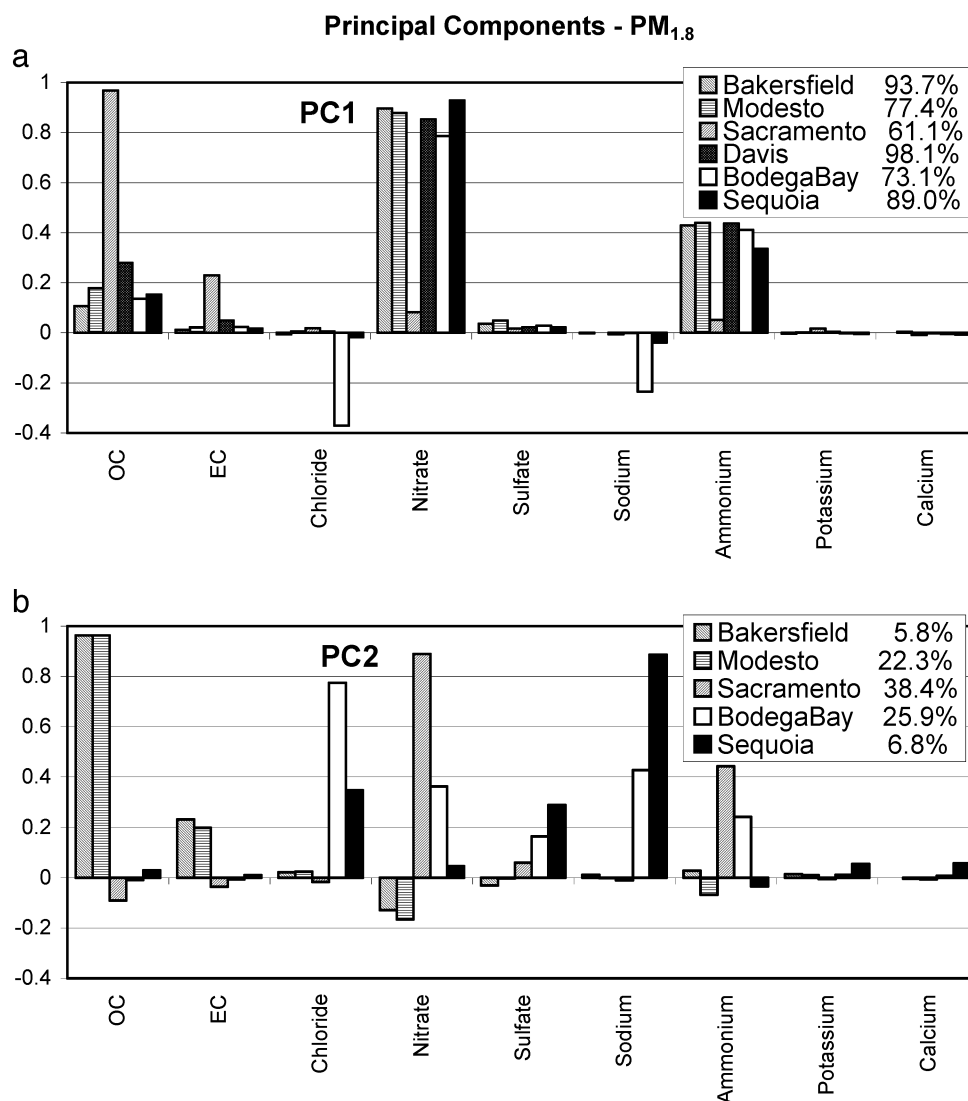
Principal Components - PM₁.₈

Figure 10. PCA of PM$_{1.8}$ concentrations at Bakersfield, Bodega Bay, Davis, Modesto, Sacramento, and Sequoia. The percentage of variance explained by each PC is shown in the key adjacent to the sampling location. The second PC is shown to explain significant residual variance not covered by the first PC.

for more than 99.5% of total variance at all but the Sequoia site. The first two PCs for the sites on the valley floor (Bakersfield, Modesto, Sacramento, and Davis) are very similar. One is dominated by NH_4^+ and NO_3^- and the other by OC and EC. At Bakersfield and Davis, PC1 is dominated by NH_4^+ and NO_3^- and constitutes 93.7 and 98.1% of total variance, respectively. At Modesto, PC1 is still dominated by NH_4^+ and NO_3^- but now accounts for only 77.4% of total variance. At Bakersfield and Modesto, the second PC is dominated by the carbon species OC and EC. At Sacramento, situated in the middle of a residential neighborhood, PC1 is dominated by the carbon species, while PC2 is dominated by NH_3 and NO_3^-. This suggests separate sources for these pollutants and some independence between them on the valley floor. The relative importance of the two dominant PCs, one with NH_4NO_3

and the other with OC and EC, appears to be dependent on the proximity to residential areas (likely associated with wood smoke). Some OC and EC also are present in PC1 at Bakersfield, Modesto, and Davis, suggesting the presence of carbon sources other than wood smoke. At Sacramento, wood smoke completely dominates the carbon signal and the NH_4NO_3 PC shows a negative correlation to carbon species.

At Bodega Bay and Sequoia, the two main PCs for the PM$_{1.8}$ size fraction suggest a different set of sources than were found on the valley floor. The main components of PC1 at both sites consist of contributions from both NH_4NO_3 and carbon species. These species are not emitted locally in great quantities but are found predominantly because of transport to these sites, mixing en route, and, therefore, arrive together. At Bodega Bay,
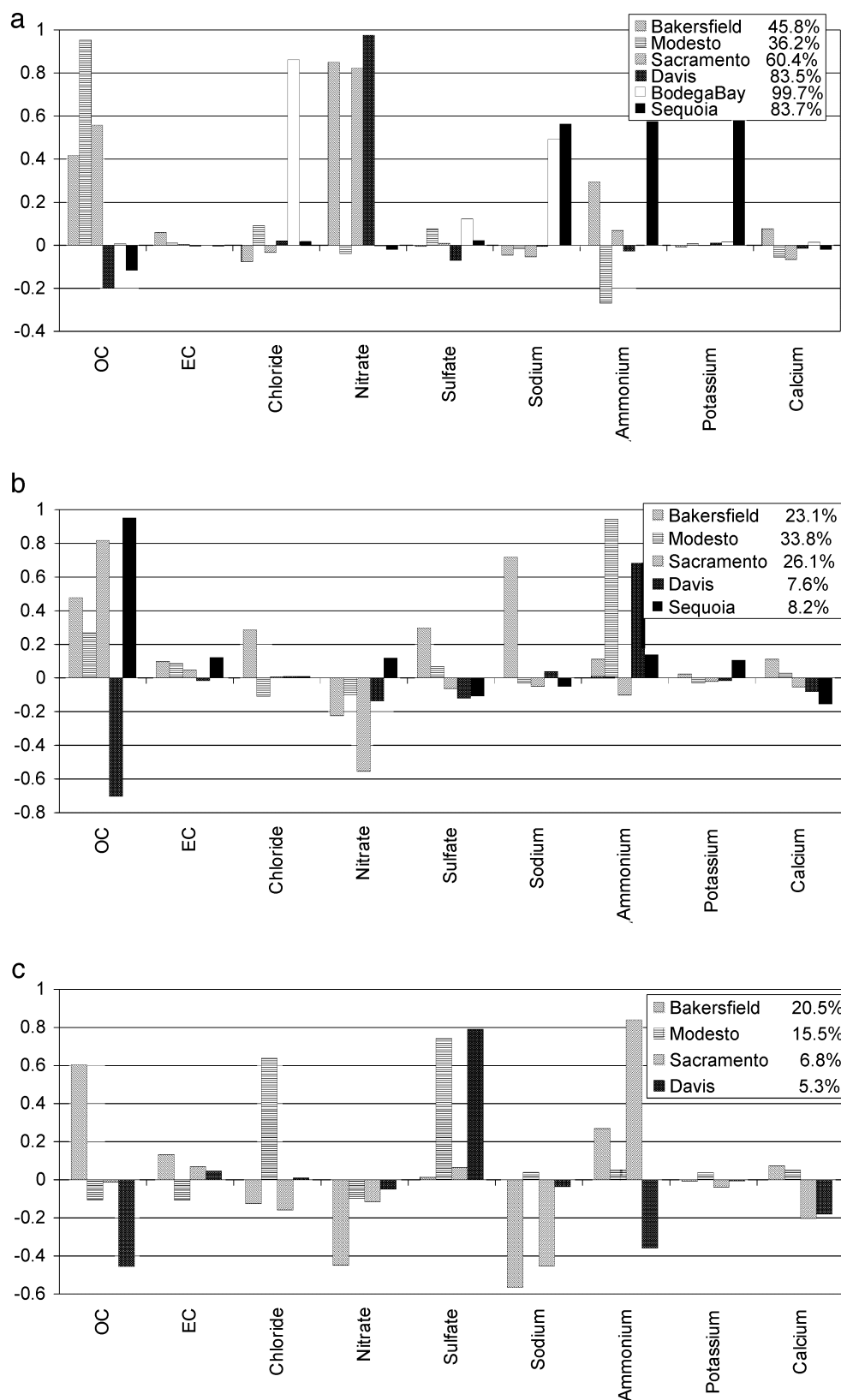
Figure 11. PCA of coarse (PM_{10}–$PM_{1.8}$) concentrations at Bakersfield, Bodega Bay, Davis, Modesto, Sacramento, and Sequoia. The percentage of variance explained by each PC is shown in the key adjacent to the sampling location. The second and third PC is shown to explain significant residual variance not covered by the first PC.

the transport of these species is likely from either farm-land directly inland or from the Central Valley, whereas at Sequoia, the transport is likely from the SJV. The second PCs at both Bodega Bay and Sequoia (PC2) consist of NaCl, nitrates, and sulfates, suggesting a sea-salt source.

The PCs for the coarse fraction of PM (Figure 11) are not as easily analyzed as the PCs for the $PM_{0.1}$ and $PM_{1.8}$ size fractions. At Bodega Bay, the first PC represents 99.7% of total variance and consists of mainly sea-salt species such as NaCl and some SO_4^{2-}. However, at the remaining sites, at least three PCs are needed to capture an aggregate 90% of the variance in the data set. There are many different sources for these particles, and some coagulation appears to have taken place to mix NH_4NO_3 and or wood smoke with road dust.

CONCEPTUAL MODEL REFINEMENT

The 24-hr NAAQS for $PM_{2.5}$ (65 µg/m^3) is clearly exceeded in the southern part of the SJV during wintertime stagnation events. By combining the knowledge gained from the size-resolved analysis, the PC analysis, and comparisons between concentrations on the valley floor versus at Sequoia (situated 415 m above the valley floor), we can add to the current conceptual model for this system. An enhanced conceptual model will help decision-makers take the most appropriate action to meet the NAAQS for PM_{10} and $PM_{2.5}$.

During the first stagnation event (IOP1–IOP3), the concentration trends of the main pollutants seen on the valley floor are not similar to trends measured at Sequoia. Maximum $PM_{1.8}$ concentrations in Bakersfield and Modesto reach 176 and 152 µg/m^3, respectively, during IOP3, while at Sequoia, the maximum $PM_{1.8}$ measured was 18 µg/m^3. Nor does $PM_{1.8}$ at Sequoia increase in a similar fashion as at Modesto and Bakersfield during IOP1–IOP3. The same argument can be made for individual constituents of $PM_{1.8}$ such as NH_4^+, NO_3^-, and carbon. These trends suggest that the valley-wide mixed layer proposed to exist during the day can have depths less than 415 m during severe air pollution events. Rawinsondes data suggest that during IOP3, the mixing layer at 4:00 p.m. was anywhere from 200 to 450 m deep, while, at other times of the day, a ground-based atmospheric inversion was in place. During the second stagnation event (IOP4), the mixing layer appears to be much higher because concentrations at Sequoia are not nearly as divergent from those on the valley floor. From January 31 to February 3, 2001, $PM_{1.8}$ increases from 34 to 89 µg/m^3 at Bakersfield and from 13 to 30 µg/m^3 at Sequoia. During this time, the NH_4NO_3 and OC show a sharp increase in concentration at Sequoia in concert with a similar increase at

Bakersfield. Hence, $PM_{1.8}$ appears to be more effectively transported to Sequoia from sources in the valley during the later air quality episode when the inversion strength was weaker. These trends suggest that, during IOP4, Sequoia was located within the SJV mixing layer. Rawinsondes data from IOP4 suggest that the mixing layer was ~800 m deep at 4:00 p.m.

Immediately after the weak upper-level disturbance on December 24, 2000, a spike in Na$^+$, Cl$^-$, and SO_4^{2-} at Bakersfield on December 26, 2000, and Sequoia on December 27, 2000, suggest that particles from the coast had managed to traverse the Coastal Range in the southern end of the SJV. No analogous signal in Na$^+$, Cl$^-$, and SO_4^{2-} was observed at the Modesto and Sacramento sites farther north. This brief signal illustrates that mixing processes aloft can transport pollutants to the southern portion of the SJV without impacting surface concentrations at the northern end of the SJV.

The breakup of an air pollution episode can provide clues about atmospheric behavior that help one to understand the general system. At the end of IOP3, the strong Great Basin High started to break up, leading to decreased PM concentrations at Bakersfield. At the same time, concentrations began to increase at Modesto, Davis, and Bodega Bay. The aerosol composition at Bodega Bay at the end of IOP3 contains a large amount of NH_4NO_3 and OC. This behavior suggests that the SJV emptied from the south, up through Modesto and Davis, and out to the coast. During the breakup of the second weaker system, concentrations decrease in the northern end of the valley at Davis and Modesto beginning on January 2, 2001, while concentrations at Sequoia and Bakersfield continued to increase through to the end of the sampling period. $PM_{1.8}$ also increased at Bodega Bay during this time, but only because of an influx of sea-salt particles. These trends suggest that, during IOP4, the valley emptied in a more typical summer fashion from the north to the south.

The temporal variation for different chemical components in different particle size fractions suggests that NH_4NO_3 concentrations build up slowly during multiweek stagnation episodes in the $PM_{1.8}$ particle size fraction. The temporal variation of carbonaceous particles in the fine and ultrafine size ranges suggests that these particles have much shorter atmospheric lifetimes. Ultrafine particles especially show clear diurnal signals (higher concentrations at night) but do not increase in concentration significantly during the multiweek stagnation episode. At the heavily polluted Bakersfield location, $PM_{0.1}$ concentrations decrease as $PM_{1.8}$ concentrations increase. This trend suggests that the dominant removal process for ultrafine particles in the SJV atmosphere is coagulation with larger particles.

CONCLUSIONS

During the period December 16, 2000–January 7, 2001, a high-pressure system situated over California produced ideal meteorological conditions for the multiweek buildup of atmospheric PM in the SJV. During this time period, typical daytime mixing depths in the SJV were less than 415 m above ground level. Fine airborne particle concentrations at Bakersfield increased from 20 to 172 $\mu g/m^3$ during this event. The majority of the fine particle mass was NH_4NO_3 driven by an excess of gas-phase NH_3.

$PM_{0.1}$ concentrations exhibited very different behavior relative to fine particle concentrations. Peak $PM_{0.1}$ concentrations were ~2.4 $\mu g/m^3$ measured at Sacramento and Bakersfield. $PM_{0.1}$ concentrations were distinctly diurnal, with daytime concentrations ~50% lower than nighttime concentrations. $PM_{0.1}$ concentrations did not accumulate during the multiweek stagnation period; rather, $PM_{0.1}$ mass decreased at Bakersfield as fine particle ($PM_{1.8}$) mass was increasing. These trends are consistent with coagulation as a dominant removal mechanism for atmospheric $PM_{0.1}$. The majority of the $PM_{0.1}$ mass was associated with carbonaceous material.

PCA reveals two distinctly different types of fine particles in the atmosphere in the SJV during high-pressure stagnation events. The first type of particle is composed mainly of carbonaceous material with very little NH_4NO_3. The smallest of these carbonaceous particles appears to dominate the $PM_{0.1}$ range. The second type of particle is composed mainly of carbonaceous material associated with NH_4NO_3. These particles likely are formed from the atmospheric transformation of the fresh carbonaceous particles.

To meet the current NAAQS for $PM_{2.5}$ during wintertime stagnation events in the SJV reductions in NH_4NO_3 will have to be achieved. At this point, the limiting component in the formation of NH_4NO_3 is HNO_3, and so reduction in NO_x or VOC will be the quickest way to achieve compliance. There is currently no standard for atmospheric $PM_{0.1}$ concentrations, but the peak $PM_{0.1}$ mass concentrations observed in the SJV during the current study are approximately twice as high as $PM_{0.1}$ concentrations measured in Los Angeles.[37] $PM_{0.1}$ in the SJV are composed almost entirely of carbonaceous aerosol likely emitted from primary combustion sources. $PM_{0.1}$ in the SJV represent a potentially serious public health threat that should be addressed.

ACKNOWLEDGMENTS

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